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**14. ABSTRACT**

The synthetic research efforts focused on three main topics: (1) a profound, detailed study of the polymerization of regioregular, head-to-tail coupled poly(alkoxythiophene)s (HTP3AOTs), (2) the development of processable, high-molecular weight polydithienopyrroles (PDTPs), (3) the construction of alternating copolymers of cyclopentadithiophene and thiophenes (P(CPDTaltT)), and (4) the development of soluble, highly ordered polythienothiophenes (PTTs). All these polymers are highly conjugated, thiophene-based polymers, with large variation in their bandgaps. In view of the important role of regioregularity in the Faraday rotation observed in thin films of polythiophenes an important part of the research effort was focused on the development of synthetic methodologies and a search of new polymers. Additionally the physico-chemical properties of several polythiophenes were investigated, with some remarkable results. Also the magnetic properties of several polythiophenes were investigated, as well as new polythiophenes synthesized. Final work involved in search for new synthetic pathways for new polythiophenes and the initiation of computer calculations/simulations to identify polymer conformations active in magnetic properties of several polythiophenes. Initial attempts were made to develop a new model based upon previous results to describe magnetic effects in organic media.

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Project:

# Chiral and highly regioregular polythiophenes
# for magneto-optics, organic magnets and ferrotoroïd materials

Grant number **FA8655-07-1-3004**

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**Abstract of proposed research effort** (as given in grant application):

*The objective of the proposed research is to elucidate the magnetic and magneto-optic properties of polythiophenes in relation with their molecular regioregularity and their supramolecular organisation in thin films. Extensive synthetic efforts will be required to analyze molecular (intrachain) structure-property relationships and assess the intricate role of supramolecular structure in defining the strong Faraday rotation observed in films of polythiophenes and related polymers. The relations between intrachain properties, such as regioregularity, bandgap structure of the polymers, aromaticity factors... etc. will be thoroughly analyzed by accurate Faraday rotation measurements and the dispersion, film processing conditions and, for chiral polythiophenes, by CD measurements.*

*We will also continue to explore the surprising discovery of a ferromagnetic transition in polythiophenes at low temperature and investigate, by using chiral polythiophenes, the possibility of ferrotoroïdiciy in these materials.*

*Also, based upon the connection between Faraday rotation and the inverse Faraday effect we will explore the possibilities of the inverse Faraday effect in films of polythiophenes using advanced laser methods enabling also the study of the dynamics of the Faraday effect.*

*In a joint collaboration with the University of Arizona, College of Optical Sciences, the newly synthesized regioregular π-conjugated polymers will be investigated for their potential applications in organic solar cells.*

*The studies proposed here may lead to new materials and with important new device applications.*

In this report period the we were mainly involved in search for new synthetic pathways for new polythiophenes and started computer calculations/simulations to identify polymer conformations active in magnetic properties of several polythiophenes. Also, we try to develop a new model based upon previous results to describe magnetic effects in organic media.

**Introduction.**

Due to problems with reproducibility of the measurements of Faraday rotation in polythiophene films we made a thorough assessment of all results previously obtained.

A very clear indication of the complexity of Faraday rotation in polythiophene films are shown by some experiments which are very critical to the phenomena observed.

First, it was noted that large Faraday rotation in spin-coated films of poly(3-octyloxy)thiophene could only be measured *if* the films were spincoated from THF-solution – other solvents yielded films which were (almost) completely inactive.

A second experiment – even more convincing of the intricate nature of the observed effects – is the measurement of Faraday rotation from thin spin-coated films of poly(cyclopentadithiophene) (PCPDT). The original films after spin coating present a blue phase with a very high Verdet constant of $2.5 \ 10^5$ °/Tm @ 670 nm. After a few days these blue films become purple and show no Faraday rotation. This effect is presumably not due to oxidation in air because the polymer redissolved has unchanged spectral properties. Most probably we have here a (supramolecular) reorganisation in the film – the blue phase a thermodynamically unstable phase – which slowly converts to the more stable purple phase. Unfortunately the unstable phase seems to be the active one in Faraday rotation!

A third series of experiments was done on poly(3-dodecylthiophene) (P3DT). Thick films (2 μm) of this polymer (high molecular weight, ~1200 monomers/chain) show a rather high Verdet constant of $2 \ 10^4$ °/Tm. After annealing these films for 12 hrs at 120°C the Faraday rotation is completely gone. Again we see transformations (reorganisation) in the film structure clearly shown by AFM pictures (see Fig. 1 and 2). In general, X-ray studies of these films confirm the breakdown of molecular organisation upon melting and melt-quenching these films.
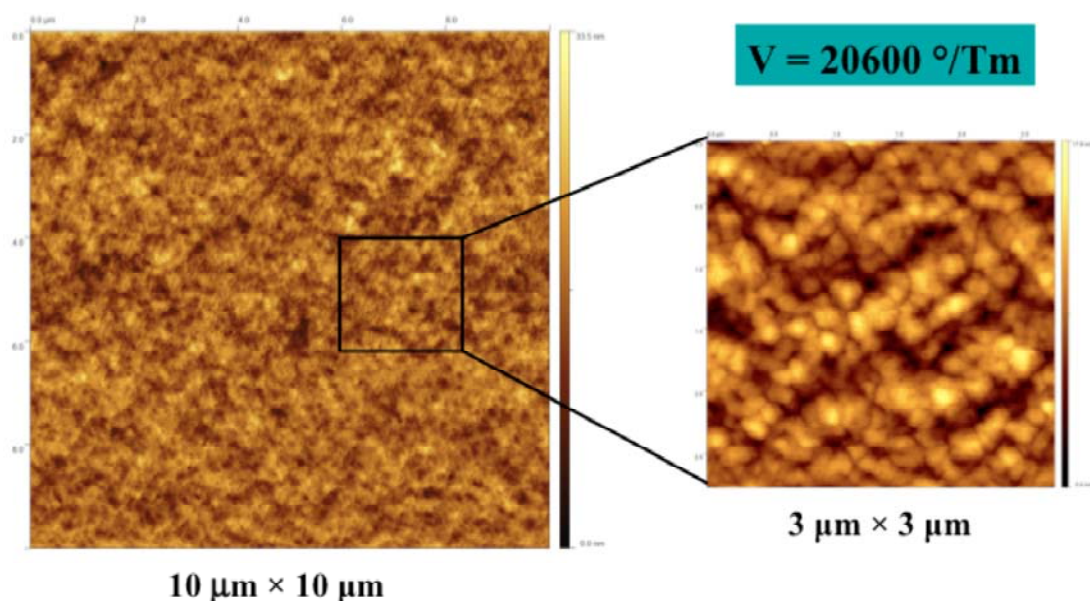
**Figure 1**. Topographic image of the surface of a thick (2 μm) film of large molecular weight P3DT (~ 1200 monomer / chain).
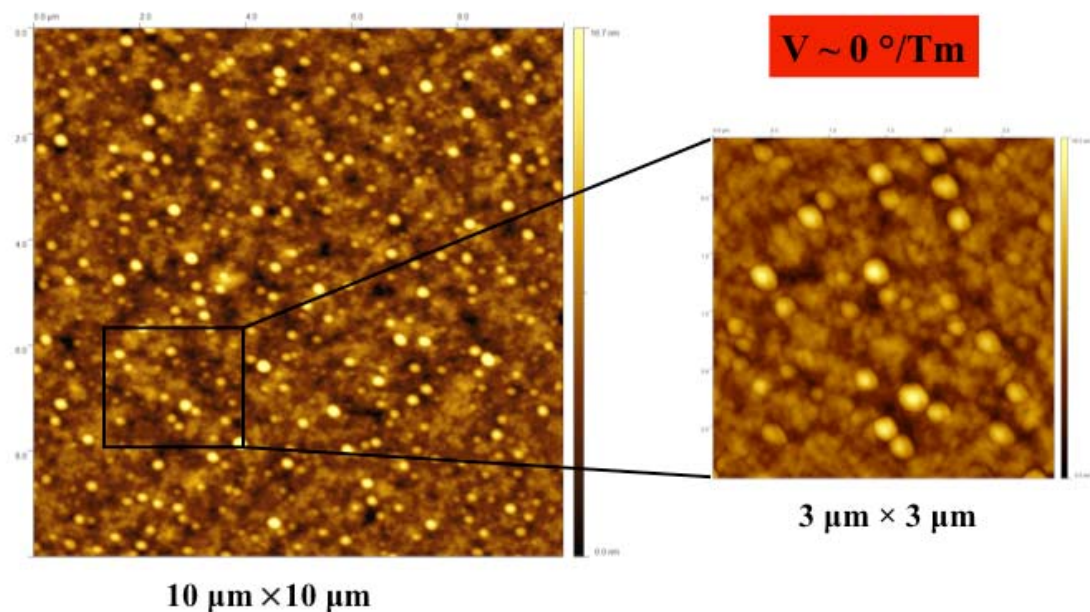


**Figure 2**. Topographic image of the surface of same thick (2 μm) film of P3DT shown in previous slide, but after annealing for 12 hrs at 120 °C; particles are of ~ 10 nm diameter!

All these (puzzling) observations have been documented in previous reports.

Now, the conclusion is emerging that the magnetic effects observed in polythiophenes (generally in conjugated polymers?) may be linked to some "active" conformations present in films. A prime target of further research should therefore be the identification of these active

conformations and, perhaps, synthesize new polymers in which these conformations are (intrinsically) stable.

In this phase of the project we therefore were working on:

1) new synthetic pathways for polythiophenes – also looking into block-copolymers

2) computer calculations/simulations (DFT) of the possible structures of pristine polythiophenes (in films, in solution..).

Computer calculations/simulations are particularly important in view of some recent Hyper-Rayleigh-Scattering (HRS) measurements from solutions of conjugated polymers which show an extreme sensitivity of HRS on the nature and permittivity of the solvent used. And since HRS is mainly determined by the symmetry of he scatterers these observations indicate a strong dependence of the conformational structure of the polymer (and polymer aggregates?) on the environment.

**Synthesis of end-capped conjugated polymers.**

The research efforts focused on the development of a general protocol for the synthesis of conjugated polymers endcapped with a functional group. The most straightforward way for this purpose is reacting a monomer, equipped with the desired functional group, with a growing polymer chain at the end of a chain-growth polymerization. However, this approach is only applicable on living polymerization and, unfortunately, the polymerization of most conjugated polymers does not fulfil this requirement. Therefore, we investigated an alternative approach is which the polymer was grown from a functionalized initiator. In that case, termination reactions do not hamper the functionalization and the protocol should therefore be applicable on a broad variety of conjugated polymers.

If the Ni-catalyzed polymerization of poly(3-alkylthiophene) is examined into more detail (Figure 3), it is clear that **2** is the actual initiator, prepared in situ from monomer **1** and Ni(dppp)Cl$_2$ (dppp = 1,3-bis(diphenylphosphinopropane)).
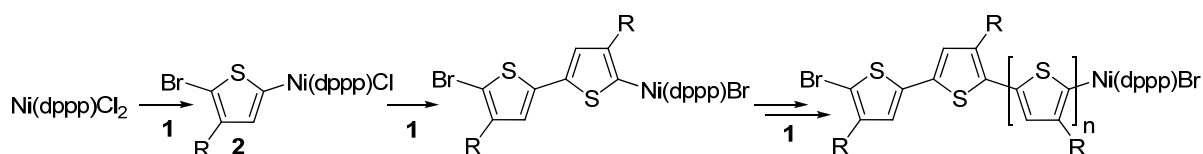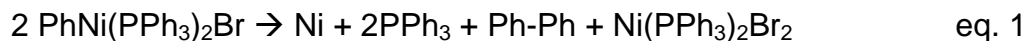


**Figure 3**. Polymerization of poly(3-alkylthiophene)s. **1** = 2-bromo-3-alkyl-5-chloromagnesiothiophene.

Suitable (functionalized) initiators should therefore be bromo(aryl nickel)complexes, ligated with two phosphor atoms. The aromatic group can possibly contain a functional group. Importantly, in order to prevent disproportionation of the aryl nickel compounds, the aryl groups must be equipped with a methyl group in *ortho*-position (equation 1).

$$2\ PhNi(PPh_3)_2Br \rightarrow Ni + 2PPh_3 + Ph\text{-}Ph + Ni(PPh_3)_2Br_2 \qquad \text{eq. 1}$$

Several (functionalized) Ni-initiators were successfully prepared and isolated (Figure 2). In a next step, these molecules were used to initiate the polymerization of various monomers, *i.e.* 3-alkylthiophenes, 3-alkoxythiophenes, 3-thioalkylthiophenes and 2,5-dialkoxyphenylenes (Table1, P1-4). In all cases, the polymerization was successful.
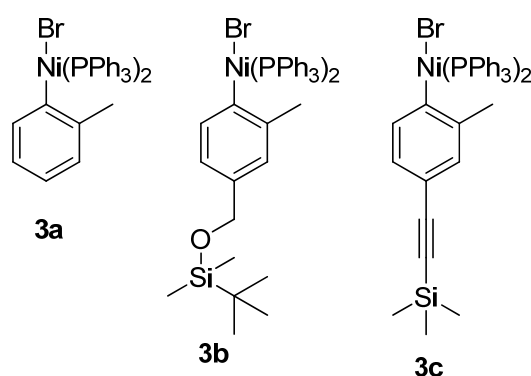


**Figure 4.** Structure of the Ni-initiators.

**Table 1.** Overview and results of the polymerizations performed.

| entry | monomer[a] | initiator | ligand added | $\overline{M}_n$ (kg/mol)[b]  GPC[c]  $^1$H NMR[d]  MALDI-ToF | end-groups[e] | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | In[f]/H | In/Br | Br/Br + Br/H + H/H | In/In |
| P1 | C₆H₁₃ ... ClMg—S—Br | **3a** | / | 3.0 (1.3)  1.7  1.8 | 65% | 15% | 20% | 0% |
| P2 | Br—S—MgCl (O-alkyl) | **3a** | / | 5.5 (1.9)  n/a  1.7 | 40% | 45% | 15% | ~0% |
| P3 | Br—S—MgCl (S-alkyl) | **3a** | / | 1.8 (1.3)  n/a  1.8 | 40% | 60% | 0% | traces |

| | Monomer | In[f] | Ligand | Mn (PDI)[c] / [e] / [d] | | | | |
|---|---|---|---|---|---|---|---|---|
| P4 | Br–C6H2(OC8H17)(OC8H17)–MgCl | 3a | 1 eq dppe[g] | 3.5 (1.2)<br>n/a<br>2.5 | h | h | h | 0% |
| P5 | ClMg–thiophene(C6H13)–Br | 3a | 1 eq dppp[i] | 3.8 (1.5)<br>1.4<br>1.7 | 85% | 5% | 10% | 0% |
| P6 | ClMg–thiophene(C6H13)–Br | 3a | 2 eq dppp | 2.6 (1.2)<br>1.8<br>1.7 | 95% | 0% | 5% | 0% |
| P7 | ClMg–thiophene(C6H13)–Br | 3b | 2 eq dppp | 3.7 (1.3)<br>2.2<br>1.9 | 95% | 0% | 5% | 0% |
| P8 | ClMg–thiophene(C6H13)–Br | 3c | 2 eq dppp | 3.2 (1.3)<br>2.1<br>1.9 | 80% | 10% | 10% | 0% |
| P9 | ClMg–thiophene(C6H13)–Br | 3a | 2 eq dppp | 2.0 (1.2)<br>n/a<br>1.8 | n/a | n/a | n/a | n/a |

[a] The monomer formation was checked by $^1$H NMR spectroscopy and found to be quantitative for P1 and P5-P9, 31% for P2, 64% for P3, 78% for P4.

[b] of the samples after washing with acetone

[c] in THF toward poly(styrene) standards. The polydispersities are given between brackets. GPC tends to give erroneous results for, for instance, P3AOTs, putting the results of P2 (and P3) into perspective.

[d] determined from the mean of the ratios of the integrals at 2.8 ppm/2.4 ppm and 7.0 ppm/6.9 ppm.

[e] determined by MALDI-ToF

[f] In = initiator

[g] dppe = 1,2-bis(diphenylphosphino)ethane

[h] The MALDI-ToF spectra indicate that two sets of polymer chains are present, Tol/X and Br/X end-capped in a 10/3 ratio, with X unknown, corresponding to a mass of 82 Da and different from Tol and Br. This shows that no disproportionation occurs, that ~80% of the chains are initiated by the Ni-initiator, but that an unknown termination reactions occurs.

[i] dppp = 1,3-bis(diphenylphosphino)propane

Detailed end group analysis was performed by Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-ToF) spectrometry. This revealed that (*i*) some Br-terminated polymer chains are present, which points at termination reactions originating from decomplexation of the Ni-moiety, (*ii*) no polymer chains with two functional groups were formed, demonstrating the absence of disproportionation and (*iii*) also polymer chains without functional group were formed, which must be initiated by the released Ni-residues.

These results suggest that the polymerization of none of the monomers is living, although it is well-known that the polymerization of poly(3-alkylthiophene)s (P3ATs) is. Since the difference between our and the established protocol is the ligand, a ligand exchange from PPh$_3$ to dppp was performed prior to the polymerization (P5-P6). This resulted in a quasi living polymerization.

Finally, the living nature of the polymerization of P3ATs was exploited by endcapping the polymer chains with 4-chloromagnesio-anisol (P9). In this way a poly(3-hexylthiophene) end-capped with a *ortho*-tolyl group (originating from the initiator) and an anisol moiety (from the end-capping agent) was formed.

In conclusion, these results show that our protocol allows the synthesis of various conjugated polymers bearing a functional end-group. If the polymerization proceeds via a living mechanism, a polymer bearing two different end groups can be prepared.

Future research will focus on the development of all-conjugated block copolymers, functionalized surfaces and functionalized nanoparticles by coupling the polymers to other polymers, surfaces or nanoparticles, respectively, by the functional groups. Such materials show great potential as magnetic and magneto-optic materials.

**Modelling, calculations and simulations.**

The observation of nano-doughnuts in spin coated films of highly regioregular P3DT – see previous report for AFM pictures – led us to try to model these structures.
As a beginning we choose a P3DT of 70 monomers to initiate DFT calculations – BP86 exchange correlation potential with the split-valence basis set of 6-31G* qualit, containing polarisation functions on non-hydrogen atoms. The DFT calculations were done on the central polythiophene core (*without* alkyl chains).
For the structure with the alkyl chains molecular mechanics MM2 approach, as implemented in the HYPERCHEM software, was used since DFT calculations are not possible for the structure containing more than 3000 atoms. These calculations were done in collaboration with Alexander Yakimansky, Russian Academy of Sciences, St. Petersburg, Russia. For DFT the program TURBOMOLE was used.
Surprisingly the helical conformation of P3DT – itself not chiral! – is rather stable. This helical structure is shown in Figure 5 with pertinent data on the helix. The exciting prospect of the existence of such conformations in polythiophenes is a possible explanation of magnetic effects in pristine polythiophenes. Indeed, such a helical structure of conjugated, conducting, polymers – with a conductivity along the chain linked to delocalized electron density – could be seen as a **nano-solenoid** in which a fluctuating magnetic moment is present due to fluctuating currents (Johnson-Nyquist currents). Important also is that the helical structure as shown is only stable if the alkyl chains are in a regioregular arrangement – no helix could be stable if the alkyl chains would be randomly organized. Remarkably, only in regioregular P3DT we observe a ferromagnetic transition below 20 K – and this important observation has very recently been confirmed by an independent research group.

We are now working on a model where we guestimate the fluctuating magnetic moment of a nanoring of silver – with (arbitrary chosen) dimensions of the nano-doughnuts observed in P3DT film. Using the current in the ring as derived from Johnson-Nyquist noise the fluctuating magnetic moment is roughly of the same order of magnitude as a Bohr magneton. The question to be addressed now is: *can we consider such a nanoring (nanostructure) as a macro-spin giving rise to magnetic properties in organic materials ?*

# A helix of 70 poly(dodecylthiophene) units, H-[C$_4$H(C$_{12}$H$_{25}$)S]$_{70}$-H
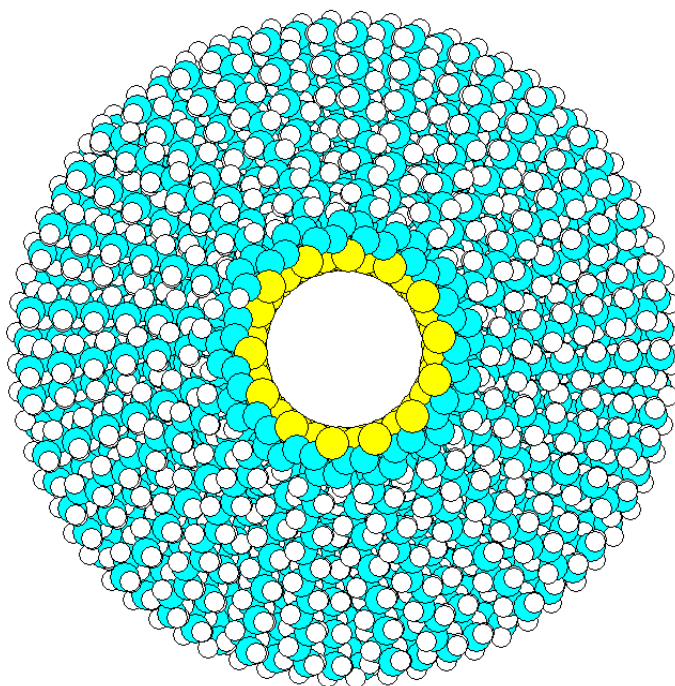
**Top view**
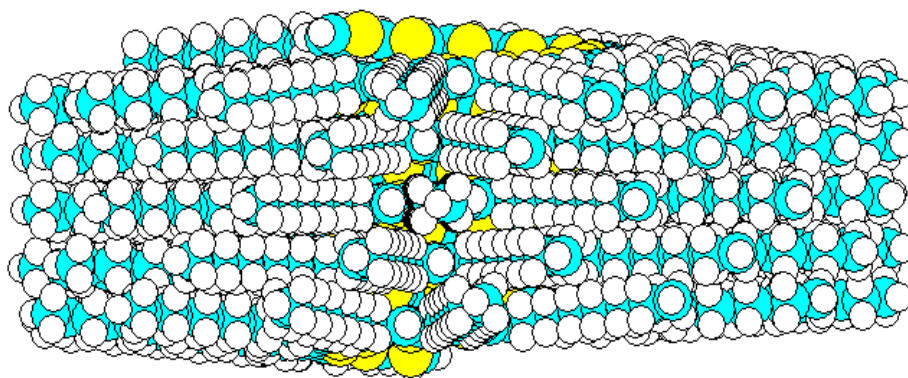
**Side view**

The polythiophene core of the helix (*without* peripheral alkyl chains, added by MM2 HyperChem) has the following approximate dimensions:

Inner diameter :  **~ 15 A**
Outer diameter:  **~ 21 A**
The length of the helix of 70 thiophene units:  **~ 17 A**

The pitch of the helix consists of **~13** thiophene units.

**Figure 5**.  Helical structure in P3DT (DFT and MM2 HyperChem calculations/simulations)

Project:

# Chiral and highly regioregular polythiophenes
# for magneto-optics, organic magnets and ferrotoroïd materials

Grant number  **FA8655-07-1-3004**

**Prof. André PERSOONS**
**Katholieke universiteit Leuven**
**Department of Chemistry**
**Celestijnenlaan 200D**
**B-3001 LEUVEN, Belgium**

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*The objective of the proposed research is to elucidate the magnetic and magneto-optic properties of polythiophenes in relation with their molecular regioregularity and their supramolecular organisation in thin films. Extensive synthetic efforts will be required to analyze molecular (intrachain) structure-property relationships and assess the intricate role of supramolecular structure in defining the strong Faraday rotation observed in films of polythiophenes and related polymers. The relations between intrachain properties, such as regioregularity, bandgap structure of the polymers, aromaticity factors... etc. will be thoroughly analyzed by accurate Faraday rotation measurements and the dispersion, film processing conditions and, for chiral polythiophenes, by CD measurements.*

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*The studies proposed here may lead to new materials and with important new device applications.*

In this report period the magnetic properties of several polythiophenes were investigated, as well as new polythiophenes synthesized.

**Synthesis and chiroptical properties of regioregular poly(alkylthiothiophene)s**

The research efforts focused on regioregular poly(alkylthiothiophene)s (P3ATTs): in a first part, the influence of the polymerization methodology on the regioregularity was investigated; while a second part dealt with the influence of the regioregularity on the chiroptical properties, which gives direct information on the molecular conformation and supramolecular structure.
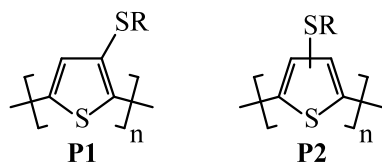


**Figure 1**: Structure of regioregular (**P1**) and regio-irregular (**P2**) P3ATTs

The influence of the polymerization methodology on the regioregularity was studied by comparing the 'modified McCullough' method and the GRIM method (Figure 2). In both methodologies, the actual monomer (thioalkyl-substituted 2-bromo-5-bromomagnesio-thiophene) is prepared in situ. The crucial difference between both methods is that the GRIM method produces both monomeric isomers (2-bromo-5-bromomagnesio-3-alkylthiothiophene and 2-bromo-5-bromomagnesio-4-alkylthiothiophene) starting from 2,5-dibromo-3-alkylthiothiophene, while in the 'modified' McCullough method, 2-bromo-4-alkylthiothiophene is converted into only one isomer, 2-bromo-5-bromomagnesio-4-alkylthiothiophene. Upon addition of the catalyst (Ni(dppp)Cl$_2$, dppp = diphenylphosphinopropane), the GRIM method produces regio-irregular P3ATTs (**P2**), while the 'modified McCullough' method renders regioregular P3ATTs (**P1**). The regiospecificity of the 'modified McCullough' method can be explained by the exclusive formation of only one isomer. The regio-irregular nature of the P3ATT prepared by the GRIM method, on the other hand, unambiguously points at the fact that both isomers are consumed during the polymerization. As a consequence, it can be concluded that – in contrast to the polymerization of 3-alkylthiophenes, but analogous to the polymerization of 3-alkoxythiophenes – the Ni-catalyst loses its regiospecificity and that the formation of regioregular P3ATTs requires the use of a polymerization method in which only one isomer is prepared.
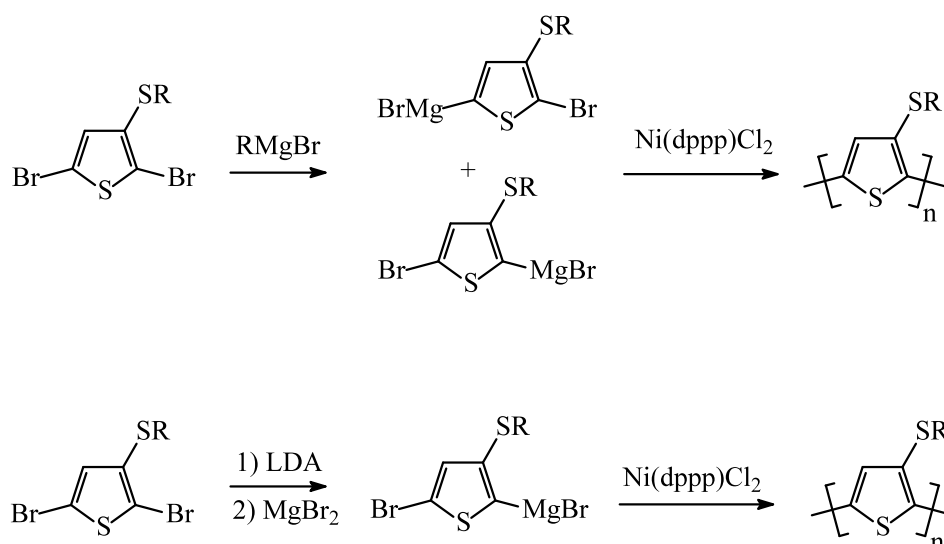
**Figure 2**: Synthesis of P3ATTs using the GRIM (up) and "modified McCullough" (down) method. LDA = lithium diisopropyl amide; dppp = 1,3-bisdiphenylphosphinopropane.

The presence of the regioselectivity of the catalyst can be explained in term of steric hindrance in the catalytic cycle of the Kumada coupling, the actual polymerization reaction (Figure 3). More in particular, the size the group directly attached to the thiophene moiety (methylene, oxygen or sulphur), is of decisive importance.
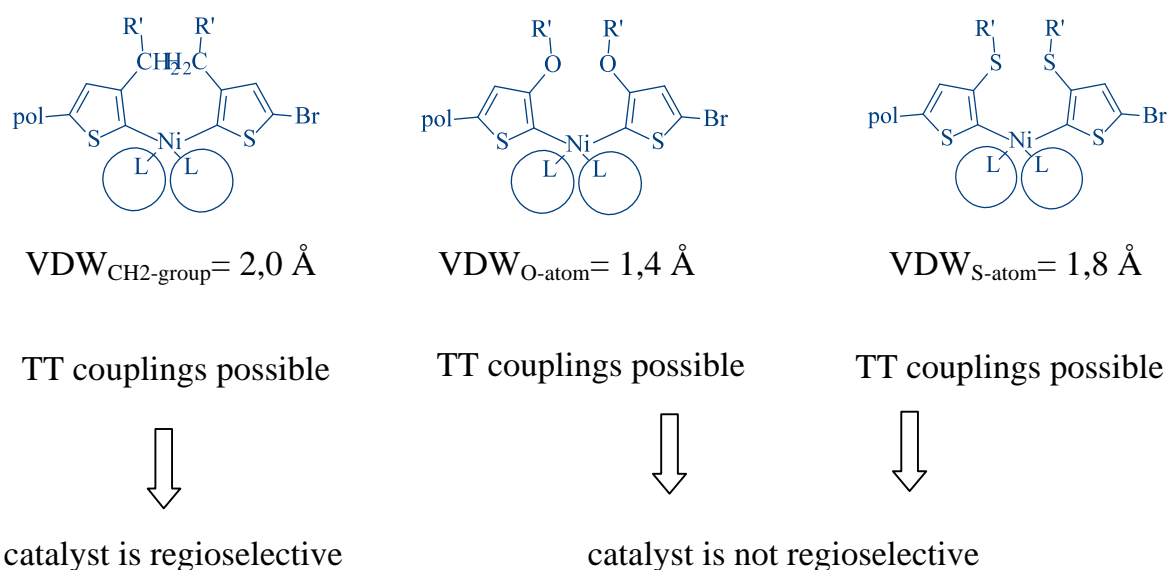


$VDW_{CH2\text{-}group} = 2,0$ Å          $VDW_{O\text{-}atom} = 1,4$ Å          $VDW_{S\text{-}atom} = 1,8$ Å

TT couplings possible          TT couplings possible          TT couplings possible

catalyst is regioselective                    catalyst is not regioselective

**Figure 3**: Explanation of the presence/absence of regioselectivity in the polymerization of poly(3-alkylthiophene)s (left), poly(3-alkoxythiophene)s (middle) and poly(3-alkylthiothiophene)s (right).

As indicated by UV-vis spectroscopy, regio-irregular P3ATTs are slightly less conjugated in solution than regioregular HT-P3ATTs, but in poor solvents and films, both polymers planarize and stack and equal conjugation lengths are observed, reflecting the possibility of P3ATTs to adopt a coplanar conformation around a HH-coupling. Remarkably, both

polymers show almost identical CD spectra, indicating that the chiral stacking is not influenced by regio-irregularity. The UV-vis spectra in poor solvents are a superposition of the π-π* transition of the polymer chains and a sharp, red-shifted band. In the CD spectra, a bisignate Cotton effect is observed in the π- π* transition, arising from chiral exciton coupling, while the red-shifted band corresponds with a monosignate Cotton effect.
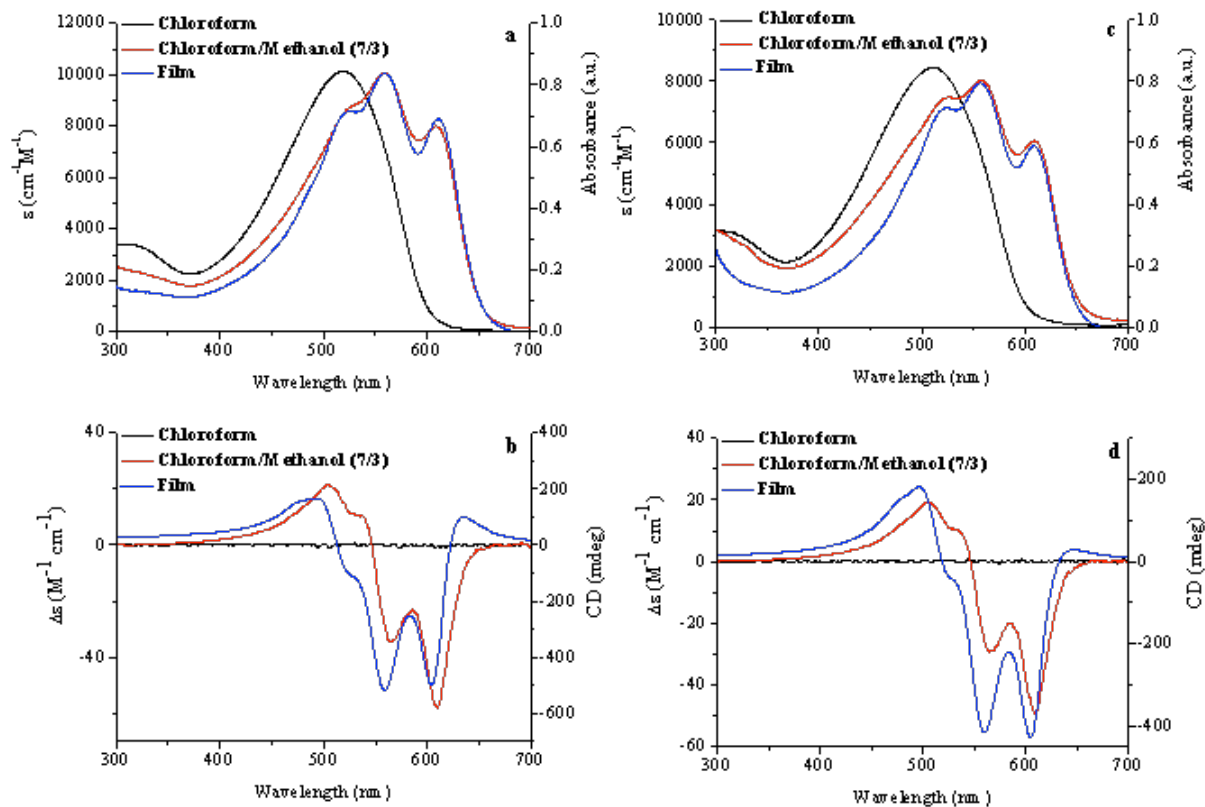


**Figure 4.** UV-vis (a) and CD (b) spectra of regioregular P3ATT; UV-vis (c) and CD (d) spectra of regioirregular P3ATT.

**Magnetic properties of poly(3-dodecyl)thiophene.**

We made further detailed measurements on magnetic properties of a poly(3-dodecyl)thiophene (P3DT, **1**) containing 70 monomers with regioregularity for the chain (without the head-group) > 99% as obtained from NMR. Regiorandom P3DT (**2**, with 50% H-T coupling) of similar molecular weight was used for comparison. **1** was found to form doughnut shaped nanostructures (Figure 5) unlike the rod and worm shaped structure previously reported albeit with larger chain lengths (> 200 monomers). Atomic force microscopy (AFM) topographic images show that the *toroid* forming the doughnut has a maximum of 9.2 nm and 22 nm as its tube and inner diameters, respectively.
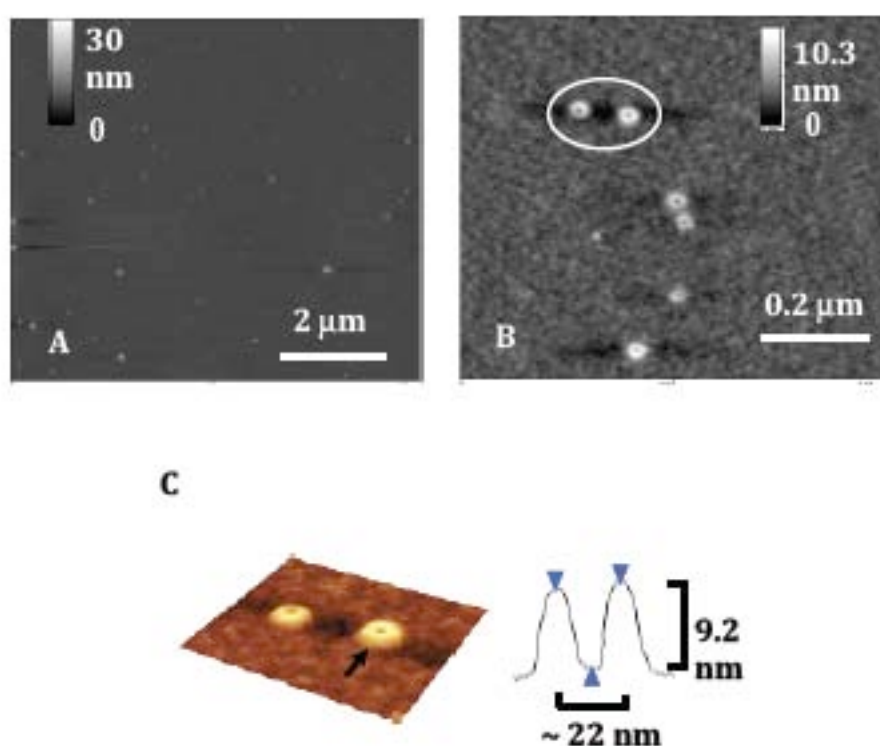


**Figure 5. A**. low resolution AFM scan of a sample of **1**. **B**. Top view of a high resolution scan of a portion of the image presented in A. **C.** scan of the doughnuts circled The scale bars at B and C are 200 nm. The scan line is a vertical cross section of the doughnut indicated by an arrow.

Although doughnuts with smaller dimensions were present, no other shape was observed. **2** was found to form fibrous structures under similar sample preparation conditions. On investigation of the magnetic properties, we found that **1** has a low temperature magnetically ordered phase (Weiss temperature, $\theta$ = 10.2 K) which is not only stable under ambient conditions but also has a very large spin quantum number, whereas **2** was found to be barely paramagnetic.

The magnetic field (H) dependence of magnetization (M) measured at several temperatures (T = 1.8 K - 20 K), shows a very fast rise at low H and reaches near saturation as early as 3 Tesla (Figure 6). Numerical fits of the M versus H/T data at 4.5 K to a percolation model give an average spin quantum number (S) of **8315**, one of the highest ever measured. However, S values and saturation magnetizations calculated at different temperatures do not scale with temperature, a behavior expected for a conventional ferromagnet. Assuming physically realistic predominantly antiferromagnetic interactions among the itinerant $\pi$-electrons and between two nearest neighbor chains, this can represent a lower bound estimate on the number of correlated electrons. In the figure 5 inset, the product $\chi T$ ($\chi$ = M/H, dc-susceptibility) of **1** and **2** are plotted as a function of T. In the case of **1** above 30 K, $\chi T$ decreases slowly, reflecting a weakly varying $\chi$, likely due to paramagnetic behavior. Below 30 K, $\chi T$ increases sharply as expected from the onset of *ferromagnetic correlation* precursive to a transition at $T_c = 16$ K.
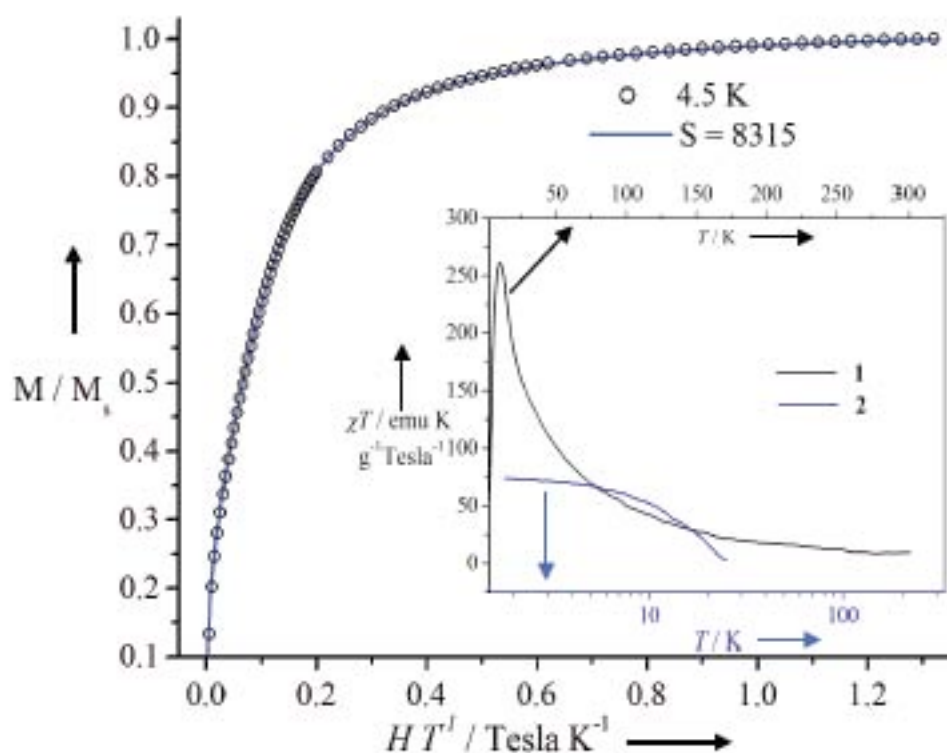


**Figure 6.** Magnetic field (H) dependence of the magnetization (M) of polymer **1** at 4.5 K, plotted as $M/M_s$ versus H/T where $M_s$ is magnetization at saturation. The solid line corresponds to the least squares fit with an average S = 8315. *Inset:* Plots of $\chi T$ of **1** and **2** versus T (top and bottom axes) where $\chi$ = M/H is the measured dc-susceptibility.

$\chi T$ was found to be field dependent, typical of a system with a large magnetic moment. The maximum at 6 K and subsequent decrease at lower temperature is a consequence of moment saturation below the Curie temperature and indicates blocking of the magnetization. The absence of high temperature susceptibility with $\theta > T_c$, though unusual for a traditional local moment ferromagnet, can be found in itinerant ferromagnets. **2** was found to possess weaker susceptibility at low temperatures and could not be measured at temperatures > 25 K. Although the possibility of an ordered phase below 1.5 K (instrumental limit) can not be ruled

out, clearly, magnetically **2** behaves very much differently from **1**. The temperature dependence of χ in **1** at low applied field (0.01 Tesla) reveal that the zero field cooled (ZFC) and field cooled (FC) magnetizations diverge below 21 K (Figure 7), again indicative of ferromagnetic correlation. Figure 8 shows magnetization hysteresis loops of polymers **1** and **2** at 1.8K measured in the field range of ± 3 Tesla. Saturation of the bulk magnetization is clearly seen over 2 Tesla of applied field. The large remnant magnetization and hysteresis in **1** are suggestive of strong ferromagnetic ordering. However, in **2**, within the experimental uncertainty of ± 2 Oe, there is no hysteresis with zero coercivity and remanence, a typically paramagnetic behavior. A closer inspection of M(H) of **1** at various temperatures below $T_c$ reveals that M is linear only at low values of H. ΔM (inset of figure 8), is defined as the magnetization range over which M is linear with H, that is ΔM is directly proportional to the spontaneous magnetization. The plot shows that ΔM drops sharply with increasing temperature, a behavior unexpected for a strong ferromagnet. For superparamagnetism, M is known to scale as H / T unlike what is seen in **1**. As for reference, a ΔM value of 1.1 emu/g at 3.5 K corresponds approximately to a moment value comparable to S=8000. The magnetic moment diameter calculated from the ΔM values at low H field and at 5 K is ~ 12 nm, comparable to the dimensions of the doughnuts of **1** measured using AFM and the grain size measured using small angle x-ray diffraction study.
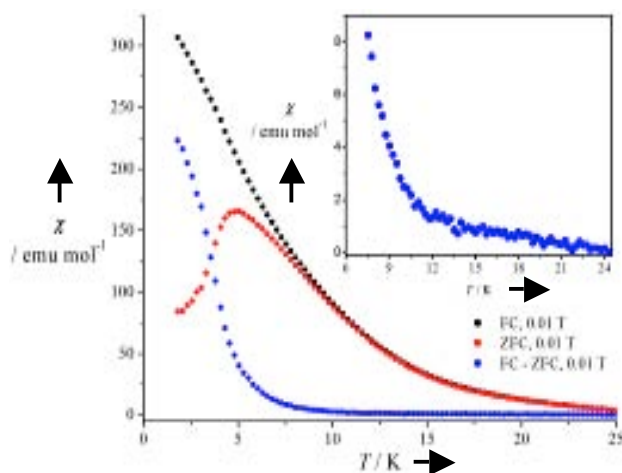


**Figure 7.** Temperature dependence of the dc-susceptibility of polymer **1** was measured with increasing temperature under 0.01 T of applied magnetic field. The sample was cooled either in zero field (ZFC) or under 0.01 T field (FC) prior to the measurement. The difference between FC and ZFC magnetization indicates the onset of divergence between the two magnetizations below 21 K. *Inset:* The differences between FC and ZFC magnetization in the temperature range of 6 – 24 K are shown.
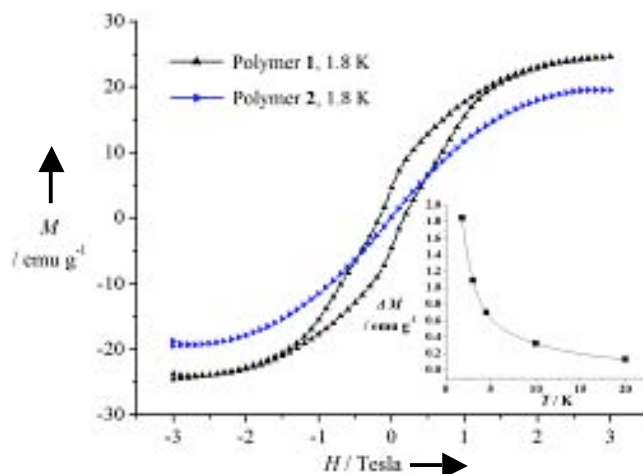
**Figure 8.** Magnetization of polymers **1** (40 mG) and **2** (132 mG) is plotted as a function of magnetic field at 1.8 K. *Inset*: ΔM versus temperature: solid line is just a guide to the eye.

To further investigate the nature of magnetic ordering in **1** we carried out ac-susceptibility measurements. The relaxation of the magnetization for **1** at low temperatures is best observed in the temperature and frequency dependence of the in-phase component of the ac-susceptibility ($\chi'$, Figure 7). The peak maximum in $\chi'$ at $T'_m$ shifts to lower temperatures and it gains in amplitude with decreasing frequency indicating the change in the blocking temperature with the angular frequency $\omega$, suggesting that the relaxation behavior is very similar to that of an insulating spin glass. However, the out-of-phase ac-susceptibility ($\chi''$) shows less pronounced frequency dependence than $\chi'$, indicating that the magnetic moments are of an interacting nature. The Figure 9 inset shows the plot of $ln\,\tau$ versus $1/T^*_m$ where $\tau=\omega^{-1}$ is the relaxation time of the magnetization and $T^*_m$ is the temperature relating to the $\chi''$ peak. The energy barrier ($E_A$) associated with the blocking and the magnitude of $\tau$ can be estimated from this plot following the Arrhenius law, $\tau = \tau_0\; e^{\left(E_A/k_B T^*_m\right)}$. Within the narrow frequency range of our measurements, the plot fits to a straight line (R = 0.997) and with an order of magnitude estimate we have $\tau_0$ = 7.8 nS and $E_A/k_B$=72 K, indicating that the system behaves as an ordered spin glass.

Detailed ICP-ES analysis was carried out on various batches of samples (result presented in Table 1) to identify any possible magnetic metal impurities and their influence on the magnetization measurements, a recurrent and major critique on observations of magnetism in organic systems. The metal analyses by ICP-ES suggest the presence of trace amounts of Ni (and Fe, Co) in both the sample and the sample holder. However, their magnetic contribution is very small, if any. For example, Ni in **1** is measured as 0.01 % which converts to a total of 6.5 μg of Ni in 65 mg of **1**. Saturation magnetization of Ni is 58.46, 58.17 and 54.69 emu/G at 4.2, 77 and 300 °K respectively. For 48 mg of **1** used in SQUID measurements, ~ 4.8 μg of Ni would give us saturation magnetization of 2.8 x 10$^{-4}$ emu. 48 mg of **1** gives us a saturation magnetization of 1.152 emu which makes the contribution of the nickel as ~ 0.024 %. Note that the temperature dependent magnetization of nickel is very different than that of **1**. The above data preclude any significant interference from magnetic metals on the reported magnetic behavior for **1**. Also note that the zero remnant magnetization and paramagnetic

nature of the regiorandom analogue clearly identifies the magnetization as a manifestation of structural ordering in **1**.
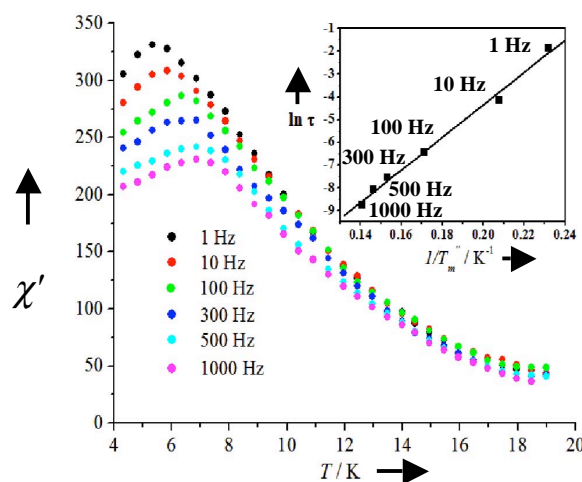


**Figure 9.** Temperature dependence of the *in-phase* ac susceptibility $\chi'$ at ac driving field of 5 Oe is shown. The measurement frequencies are indicated. ***Inset***: Arrhenius plot of the natural logarithm of relaxation time as a function of $T_m''$ (K$^{-1}$) calculated from the *out-of-phase* susceptibility ($\chi''$) data; the solid line is a linear fit of the data.

**Table 1.** ICP-ES data of RRP3DT and non magnetic sample holder used for SQUID measurements

| Sample | Iron % (w/w) | Cobalt % (w/w) | Nickel % (w/w) |
|---|---|---|---|
| RRP3DT (65 mg) | <0.01 | <0.005 | 0.010 |
| Sample holder (72 mg) | <0.003 | <0.002 | <0.002 |

Athough the exact origin of the magnetic ordering in **1** remains an open question, the role of frustration in spin polarization on sulphur in thiophene rings and an increased $d\pi$-$p\pi$ spin orbit interaction in overall magnetic ordering is an intriguing possibility. Another plausible mechanism is the possibility of coexistence of partially flat and dispersive bands in these strongly correlated electronic systems, resulting in the so-called 'flat band ferromagnetism', suggested recently. Such a conjecture can be further supported by recent observation of negative magnetoresistance at low temperatures in a shorter chain polythiophene derivative. On the other hand, at low temperature the entire 3D organization typical of RR polythiophene may have collapsed causing self doping and defect induced residual magnetism.

Electron spin resonance measurements show a spin concentration of 5 10$^{13}$ spins/g in **1**. Such a low spin concentration cannot account for the susceptibility of **1**. We believe that the *nano confinement* of itinerant $\pi$-electrons of regioregular polythiophene in an anisotropic structure such as a doughnut may be the main origin. With thermal chaos down to a minimum, spontaneous alignment among the toroidal moments generated from the nano doughnuts is a

strong possibility for creation of magnetic ordering in P3DT. For example, magnetic moment generated from the toroidal current within the doughnuts, equivalent to spatio-temporal fluctuations in the electron density in the polymer chains forming the doughnut, can be estimated as $\mu = ne_0 V_F S / 2\pi R$, where $n$ and $e_0$ are the number of torroidic electrons and electronic charge respectively, $V_F$ is the Fermi velocity (estimated as 4 x $10^6$ m/s, analoguous to metals) and R is the radius of the torroid. With R $\approx$ 11 nm and aproximately a torroidal current of 5 electrons, $\mu$ can be estimated as 2 x $10^{-20}$ $JT^{-1}$ or 2000 $\mu_B$ i.e. an average $S=1000$, a comparable estimate to that obtained from experimental data. At applied magnetic field of 0.01T (Fig. 6), $\mu H/k_B$ = 14 K, which is within the ferromagnetic transition temperature at 20 K observed in fig. 7 and 9.

We are at present performing a detailed comparative study of structural, magnetic and electronic properties of **1** in order to determine more precisely the origin of the magnetic behavior reported here as well as developing models with a nanostructural basis for organic magnetism.

*To our knowledge, there is no other purely organic stable polymer system reported to date that displays magnetic ordering in the nano regime.*

This work will be submitted to *Chemistry of Materials.*

Progress Report **15 August 2008 to 15 February 2009**

Project:

# Chiral and highly regioregular polythiophenes

# for magneto-optics, organic magnets and ferrotoroïd materials

Grant number  **FA8655-07-1-3004**

**Prof. André PERSOONS**
**Katholieke universiteit Leuven**
**Department of Chemistry**
**Celestijnenlaan 200D**
**B-3001 LEUVEN, Belgium**

**Abstract of proposed research effort** (as given in grant application):

*The objective of the proposed research is to elucidate the magnetic and magneto-optic properties of polythiophenes in relation with their molecular regioregularity and their supramolecular organisation in thin films. Extensive synthetic efforts will be required to analyze molecular (intrachain) structure-property relationships and assess the intricate role of supramolecular structure in defining the strong Faraday rotation observed in films of polythiophenes and related polymers. The relations between intrachain properties, such as regioregularity, bandgap structure of the polymers, aromaticity factors... etc. will be thoroughly analyzed by accurate Faraday rotation measurements and the dispersion, film processing conditions and, for chiral polythiophenes, by CD measurements.*
*We will also continue to explore the surprising discovery of a ferromagnetic transition in polythiophenes at low temperature and investigate, by using chiral polythiophenes, the possibility of ferrotoroïdiciy in these materials.*
*Also, based upon the connection between Faraday rotation and the inverse Faraday effect we will explore the possibilities of the inverse Faraday effect in films of polythiophenes using advanced laser methods enabling also the study of the dynamics of the Faraday effect.*
*In a joint collaboration with the University of Arizona, College of Optical Sciences, the newly synthesized regioregular π-conjugated polymers will be investigated for their potential applications inorganic solar cells.*
*The studies proposed here may lead to new materials and with important new device applications.*

## Work performed in report period.

In this report period the physico-chemical properties of several polythiophenes were investigated, with some remarkable results.

First, the newly synthesized poly(3-alkylthiothiophene)s were characterized in their (chiro)optical properties. As indicated by UV-vis spectroscopy, regio-irregular P3ATTs are

slightly less conjugated in solution than regioregular HT-P3ATTs, but in poor solvents and films, both polymers planarize and stack and equal conjugation lengths are observed, reflecting the possibility of P3ATTs to adopt a coplanar conformation around a HH-coupling. Remarkably, both polymers show almost identical CD spectra, indicating that the chiral stacking is not influenced by regio-irregularity. The UV-vis spectra in poor solvents are a superposition of the π-π* transition of the polymer chains and a sharp, red-shifted band. In the CD spectra, a bisignate Cotton effect is observed in the π- π* transition, arising from chiral exciton coupling, while the red-shifted band corresponds with a monosignate Cotton effect.

In our investigation of the mechanism behind the strong Faraday effect in conjugated polymers we focused mainly on regioregular poly(3-alkylthiophene)s because the relative ease of their preparation and their good stability. Most poly(3-alkylthiophene)s show a Verdet constant in the order of $10^4$ °/Tm, while the polymers synthesized in our group are consistently better than commercial polymers.

A new, and unexpected phenomenon was observed while investigating a thin film of poly(3-dodecylthiophene) with AFM. Films from P3DT with about 40 – 70 monomers and *highly* regioregular show a remarkable structure at the nanoscale never seen before: *we observe "doughnut" structures at the nanoscale*.
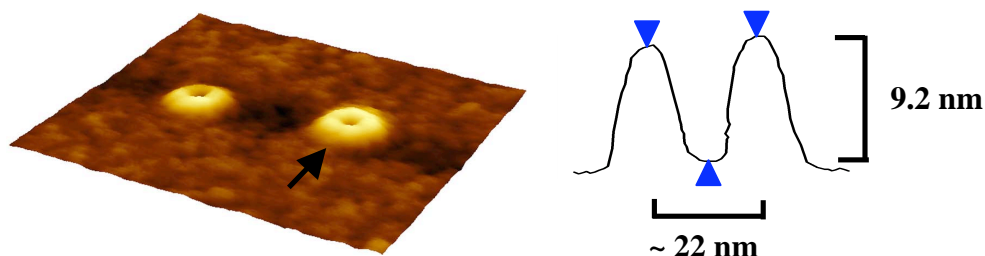


Figure 1. False color AFM topographic image of RR-P3DT doughnuts. The scan line shown at the right side is a vertical cross section of the doughnut indicated by an arrow.

From the physical dimensions as obtained from the AFM data we estimate less than 20 polymer chains per doughnut. The remarkable fact is that P3DT with larger molecular weight are known to form rod-like nanostructures. It is also clear that the physical properties of the P3DT films will be strongly affected by the required 2D bending of the polymer lamella structure in the doughnut. A better understanding of these doughnut structures will require a knowledge of the 3D organisation – it is yet unknown wether we have half or full doughnuts. In the following period we will intensely investigate these new structures to assess their role in the magnetic properties of the polythiophenes. It has not escaped our attention that these doughnut structure could be basic for a nanotoroïd, -with implications for ferrotoroidicity at the nanoscale –a key element for metamaterials with optical properties in the visible.

Concommitantly the experimental set-up to measure the Faraday rotation in thin films has been much improved in a joint effort with the Tucson group. The set-up mostly used for accurate measurements is given in Figure 1. The built-in feedback enables auto-balancing and provides up to 50 dB of CMRR. Together with a 20 dB enhancement of the modulated signal by AC coupled preamplification and low phase noise from the custom built solenoids (and power supply) yield very accurate results.
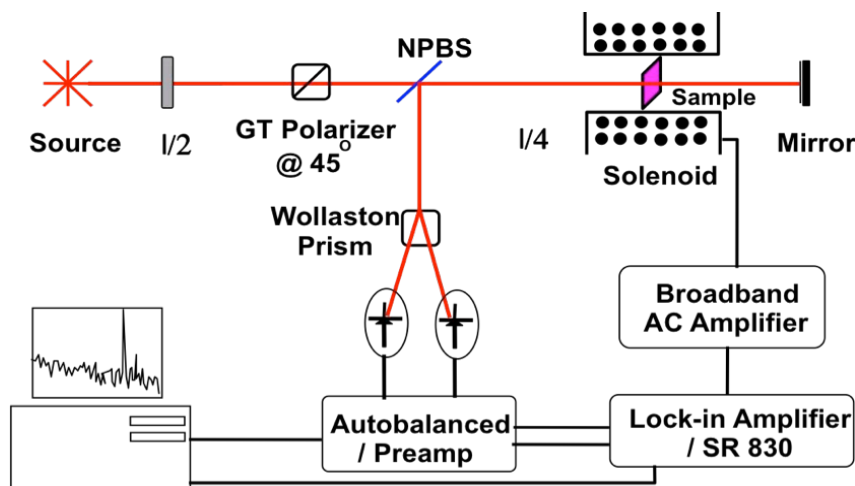


Figure 2. Experimental set-up for the measurement of Faraday rotation in thin films.

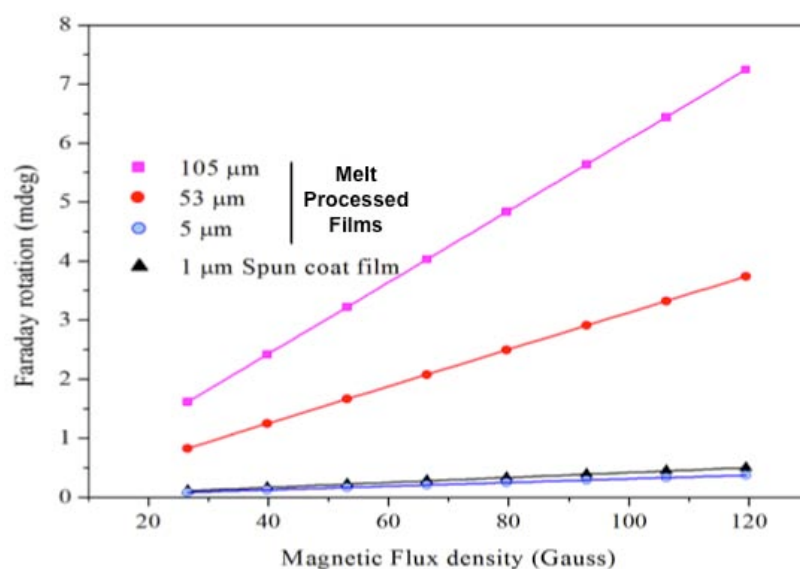The quality of the measurements are shown in Figure 3.



Figure 3. Faraday measurements on RR P3DT films (melt processed) with different thickness.

Progress Report **1 March to 15 August 2008**

Project:

# Chiral and highly regioregular polythiophenes

# for magneto-optics, organic magnets and ferrotoroïd materials

Grant number  **FA8655-07-1-3004**

**Prof. André PERSOONS**
**Katholieke universiteit Leuven**
**Department of Chemistry**
**Celestijnenlaan 200D**
**B-3001 LEUVEN, Belgium**

**Abstract of proposed research effort** (as given in grant application):

*The objective of the proposed research is to elucidate the magnetic and magneto-optic properties of polythiophenes in relation with their molecular regioregularity and their supramolecular organisation in thin films. Extensive synthetic efforts will be required to analyze molecular (intrachain) structure-property relationships and assess the intricate role of supramolecular structure in defining the strong Faraday rotation observed in films of polythiophenes and related polymers. The relations between intrachain properties, such as regioregularity, bandgap structure of the polymers, aromaticity factors... etc. will be thoroughly analyzed by accurate Faraday rotation measurements and the dispersion, film processing conditions and, for chiral polythiophenes, by CD measurements.*
*We will also continue to explore the surprising discovery of a ferromagnetic transition in polythiophenes at low temperature and investigate, by using chiral polythiophenes, the possibility of ferrotoroïdiciy in these materials.*
*Also, based upon the connection between Faraday rotation and the inverse Faraday effect we will explore the possibilities of the inverse Faraday effect in films of polythiophenes using advanced laser methods enabling also the study of the dynamics of the Faraday effect.*
*In a joint collaboration with the University of Arizona, College of Optical Sciences, the newly synthesized regioregular π-conjugated polymers will be investigated for their potential applications inorganic solar cells.*
*The studies proposed here may lead to new materials and with important new device applications.*

## Work performed in report period.

In view of the important role of regioregularity in the Faraday rotation observed in thin films of polythiophenes an important part of the research effort was focused on the development of synthetic methodologies and a search of new polymers.

High molecular weight polycyclopentadithiophene (PCPDT, see Figure 1), which should have an intrinsic regioregularity, were synthesized and their Faraday rotation measured in thin films.
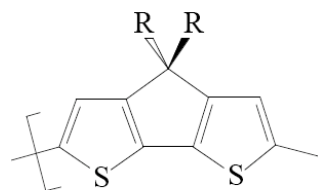


**Figure 1**: Structure of the PCPDT (see progress report August 2007).

These blue colored films are highly Faraday active with a Verdet constant of $2.5 \cdot 10^5$ °/Tm at 670 nm but gradually turn purple over time with a concommitant loss of Faraday activity. This clearly points to the role of supramolecular organisation and important questions here is the possibility of phase transition and how to stabilize the active phase.

The strongest Faraday rotation ever observed was in films of poly(alkoxythiophene)s (HT-P3AOTs). Unfortunately these polymers are (very) difficult to synthesize and are moreover not very stable. As an alternative we focused the research effort in this period on regioregular poly(alkyl**thio**thiophene)s (P3ATTs): in a first part, the influence of the polymerization methodology on the regioregularity was investigated; after mastering the synthetic procedures we will investigated the influence of the regioregularity on the chiroptical properties, which will give direct information on the molecular conformation and supramolecular structure.
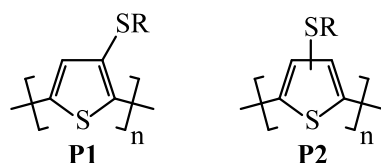


**Figure 2**: Structure of regioregular (**P1**) and regio-irregular (**P2**) P3ATTs

The influence of the polymerization methodology on the regioregularity was studied by comparing the 'modified McCullough' method and the GRIM method (Figure 3). In both methodologies, the actual monomer (thioalkyl-substituted 2-bromo-5-bromomagnesio-thiophene) is prepared in situ. The crucial difference between both methods is that the GRIM method produces both monomeric isomers (2-bromo-5-bromomagnesio-3-alkylthiothiophene and 2-bromo-5-bromomagnesio-4-alkylthiothiophene) starting from 2,5-dibromo-3-alkylthiothiophene, while in the 'modified' McCullough method, 2-bromo-4-alkylthiothiophene is converted into only one isomer, 2-bromo-5-bromomagnesio-4-alkylthiothiophene. Upon addition of the catalyst (Ni(dppp)Cl$_2$, dppp = diphenylphosphinopropane), the GRIM method produces regio-irregular P3ATTs (**P2**), while the 'modified McCullough' method renders regioregular P3ATTs (**P1**). The regiospecificity of the 'modified McCullough' method can be explained by the exclusive formation of only one isomer. The regio-irregular nature of the P3ATT prepared by the GRIM method, on the

other hand, unambiguously points at the fact that both isomers are consumed during the polymerization. As a consequence, it can be concluded that – in contrast to the polymerization of 3-alkylthiophenes, but analogous to the polymerization of 3-alkoxythiophenes – the Ni-catalyst loses its regiospecificity and that the formation of regioregular P3ATTs requires the use of a polymerization method in which only one isomer is prepared.
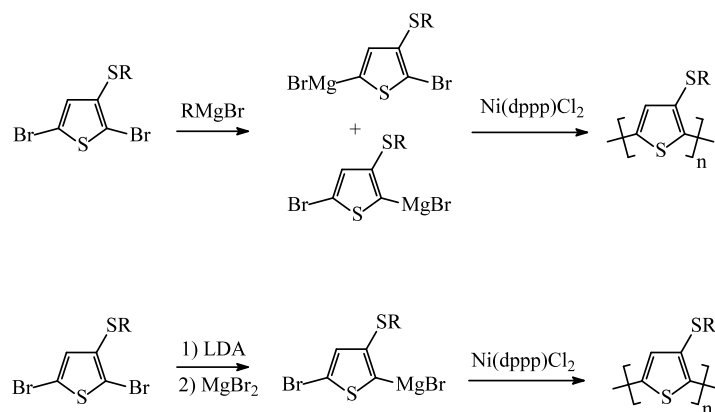


**Figure 2**: Synthesis of P3ATTs using the GRIM (up) and "modified McCullough" (down) method. LDA = lithium diisopropyl amide; dppp = 1,3-bisdiphenylphosphinopropane.

The presence of the regioselectivity of the catalyst can be explained in term of steric hindrance in the catalytic cycle of the Kumada coupling, the actual polymerization reaction (Figure 3). More in particular, the size the group directly attached to the thiophene moiety (methylene, oxygen or sulphur), is of decisive importance.
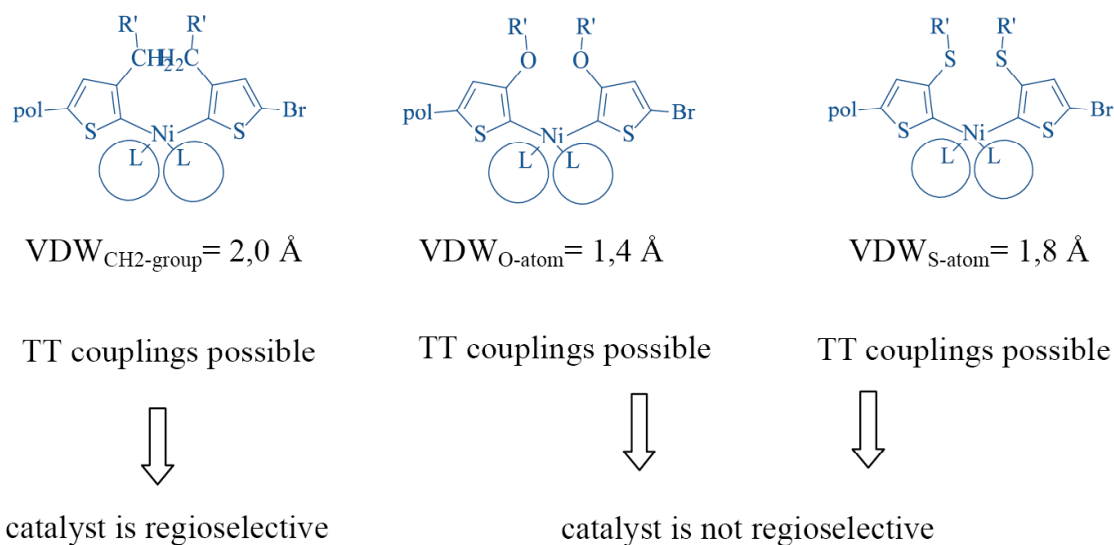


**Figure 3**: Explanation of the presence/absence of regioselectivity in the polymerization of poly(3-alkylthiophene)s (left), poly(3-alkoxythiophene)s (middle) and poly(3-alkylthiothiophene)s (right).

Final scientific Report **1 March 2007 to 29 February 2008**

Project:

## Highly Regioregular Polythiophenes for magneto-optical Applications

Grant number  **FA8655-07-1-3004**

**Prof. André PERSOONS**
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**Abstract of proposed research effort** (as given in grant application):

*The main objective of the proposed research is to create new optimized π-conjugated polymers – with a focus upon polythiophenes and analogues – that have high Verdet constants (large Faraday rotation), low optical loss in the wavelength region(s) of interest, excellent thermal and environmental stability, and good processability. In order to understand the high Faraday rotation we recently discovered in this class of polymers key structure-property relationships will be investigated by varying the chemical composition of side chains and changing the aromatic moieties in the π-conjugated chain.*
*Concomitantly the possibilities of these regioregular π-conjugated polymers for organic solar cells and for new material applications will be investigated.*

# *Work performed.*

## 1.  Synthesis of polythiophenes and analogues

The synthetic research efforts focused on three main topics: (1) a profound, detailed study of the polymerization of regioregular, head-to-tail coupled poly(alkoxythiophene)s (HT-P3AOTs), (2) the development of processable, high-molecular weight polydithienopyrroles (PDTPs), (3) the construction of alternating copolymers of cyclopentadithiophene and thiophenes (P(CPDT*alt*T)), and (4) the development of soluble, highly ordered polythienothiophenes (PTTs). All these polymers are highly conjugated, thiophene-based polymers, with large variation in their bandgaps.
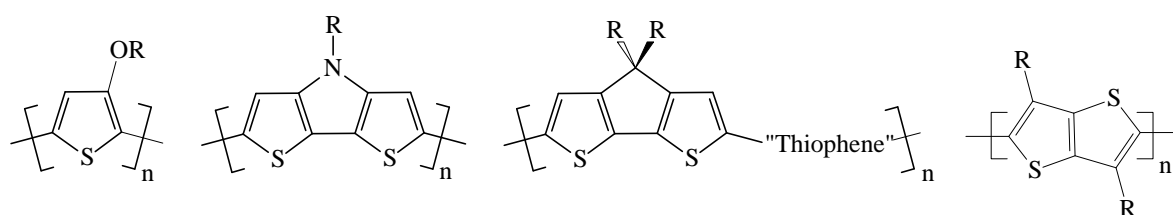
**Figure 1**:  Structure of HT-P3AOTs, PDTPs, P(CPDT*alt*T) and PTTs.

Since highly regioregular P3AOTs – in particular poly(octyloxythiophene) - show the highest Verdet reported for any conjugated polymer, we wanted to focus our research activities concerning the influence of the film forming conditions, annealing, … on these polymers. Unfortunately, while the synthesis of regioregular poly(*alkyl*thiophene)s and their monomers is robust and well-established, the preparation of HT-PAOTs suffered from monomer decomposition and low yields.  Quite often, no or only very small quantities of polymer, albeit regioregular, was obtained.

First, the origin of the regioregularity of the "modified McCullough" methodology was investigated. We had already indicated that – in contrast to the polymerization of poly(*alkyl*thiophene)s – the Ni-catalyst employed loses its regiospecificity.  Consequently, the production of regioregular, HT-P3AOTs requires the formation of only one isomer of the actual monomer.  Detailed NMR studies confirmed that in all the steps of the polymerization procedure only one isomer is formed and that no scrambling of the actual monomer occurs at conditions, which mimics the polymerizations conditions.

Next, it was tried if the actual monomer can be prepared, still as only one isomer, using other methodologies which are easier to carried out (GRIM, "modified GRIM").  In all attempts, regiorandom polymers were formed and NMR experiments demonstrated the formation of two isomers, indicating the necessity to use the "modified McCullough" methodology for the production of HT-P3AOTs.

Finally, the polymerizations conditions and monomer formation were systematically varied, in order to increase the reproducibility and yield of the monomer formation and polymerization.  While these efforts were rather successful for the monomer synthesis and the polymerization's reproducibility, the polymerization mechanism is still not perfectly understood and the yields remain low.  Intensive efforts to overcome these drawbacks are ongoing.

Secondly, soluble, processable polydithienopyrroles (PDTPs) were prepared.  Most PDTPs known were electrochemically prepared and often insoluble.  Some poorly soluble PDTPs were reported – they were usually oxidatively prepared (by addition of a chemical oxidant) - but these materials suffered from low yields, showed low molecular weights and often a poor processability.    Moreover,   since   their   polymerization   methodology   shows   limited

regiospecificity, the presence of unwanted couplings which disturb the conjugation and/or might lead to crosslinking, cannot be excluded. We hypothesized that there are two possible reasons for the poor solubility and low-molecular weight of the polymers and their low yields. The first one is the nature of the polymerization process (oxidatively), in which the polymers are prepared in their oxidized, less soluble state. Moreover, some cross-linking cannot be excluded. These problems can be circumvented by the use of organometallic-catalyzed reactions, in which the polymers are grown in their neutral form in a fashion, determined by the substitution pattern of the functional groups on the monomers. A second reason can be the $\pi$-stacking between the polymer backbones, which is probably too strong in the polymers. The use of bulky groups would reduce the $\pi$-stacking and therefore increase the solubility.

Therefore, we performed a systematic study, in which the (bulkiness of the) substituent was varied (Figure 2), as well as the polymerization method. This study revealed that increasing the bulkiness of the substituent dramatically increased the solubility and molecular weight of the polymers, but simultaneously *increased* $\lambda_{max}$. This clearly indicates that in these polymers the conjugation is not disrupted by bulky substituents, but instead that the maximal conjugation length is not reached in low-molecular weight material. Fluorescence spectroscopy experiments, in particular the Stokes shifts and fwhm, indicated that the polymer adopts rigid macromolecular structures, even in solution.
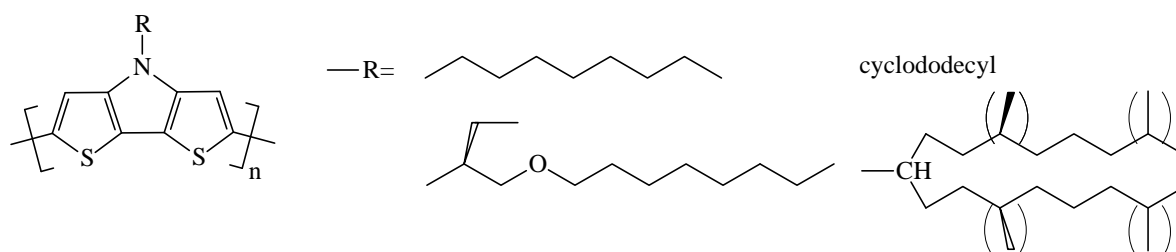


**Figure 2**: Structure of the PDTPs.

Concerning the polymerization methodology, the polymers were both oxidatively polymerized (by addition of an oxidant, in casu RuCl$_3$) and using Stille-coupling reactions. This indicated that the use of Stille-reactions dramatically increases the yield, the molecular weight and decreases the polydispersity, indicated its superiority compared with oxidative polymerizations.

Also chiral substituents were implemented. In good solvents (chloroform, THF), no Cotton effects are observed. Upon addition of nonsolvents (methanol), relative small but clear bisignate Cotton effects appear. These results are indicative for a chiral, supramolecular stacking of coplanar strands. The relative small magnitude of the Cotton effects can be explained by the fact that supramolecular stacking is complicated by the bulky substituent. Essentially the same results are obtained in film. Finally, higher molecular weight polymers more poorly aggregate than lower-molecular weights materials.

It can be concluded that by a proper choice of the substituent (bulky groups) and polymerization methodology (Stille-couplings), soluble, high-molecular weight PDTPs can be prepared in high yields. In solution, the polymer strands adopts a rigid, planar, highly conjugated conformation. Increasing the bulkiness of the substituent and molecular weight complicated efficient aggregation. This study has made PDTPs applicable in the field of magneto-optical effects, such as Faraday rotation.

A third class of polymers that have been developed are homopolymers of cyclopentadithiophene and alternating copolymers of cyclopentadithiophene and thiophenes. The substituted cyclopentadithiophene moiety was incorporated to introduce solubility and processability. The excellent solubility of the polymers containing this moiety is not only due to the presence of the substituents, but also to the fact that the substituents are oriented perpendicular to the main chain. Furthermore, the planarity of the system allows efficient conjugation.

In contrast to their benzene-analogues, polyfluorenes, homopolymers of (achiral) cyclopentadithiophene have shown *not* to aggregate. To further confirm this, a chiral poly(cyclopentadithiophene) was synthesized. The very large $\lambda_{max}$, both in solution and in film, together with their small Stokes shifts and fwhm, point at a planar, highly conjugated structure of the polymer backbone, even in solution. The absence of a red-shift upon transition to film and Cotton effects confirmed that no (chiral) aggregation takes place. It can be concluded that poly(cyclopentadithiophene)s are present as rigid rods, which do not aggregate.

Since the supramolecular structure of conjugated polymers is of tremendous importance for their electronic and optical properties and is very likely to affect their Faraday rotation, we wanted to prepare poly(cyclopentadithiophene)s, in which the electronic properties resemble those of the homopolymers, but which *do* aggregate. This has been done by alternating copolymerization of cyclopentadithiophene with planar, thiophene-based (in order to match the electronic properties of cyclopentadithiophene as close as possible) moieties. In order to be able to probe supramolecular chirality (CD), both achiral and chiral substituents were employed. These alternating copolymers were prepared using Stille-couplings.
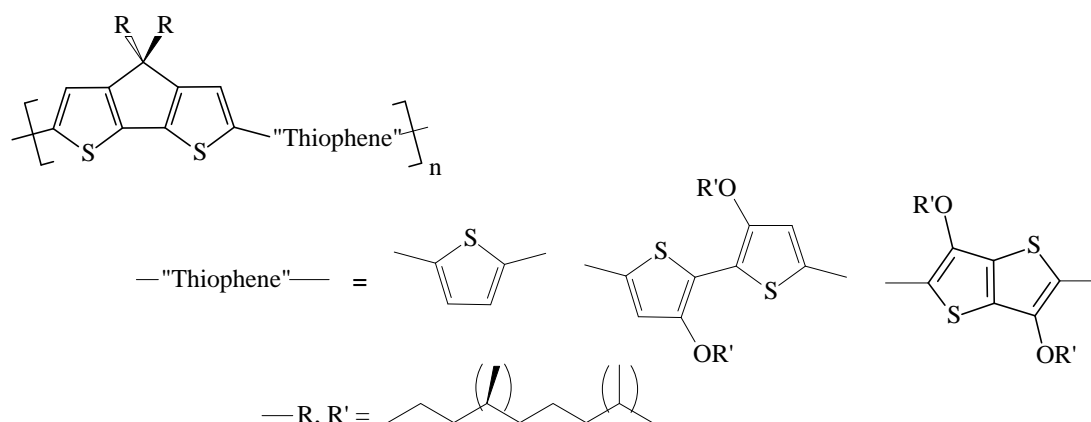


**Figure 3**: Structure of the alternating copolymers of cyclopentadithiophene and thiophene-based moieties.

Our results indicate that $\lambda_{max}$ is in most cases only slightly affected by the introduction of moieties, other than cyclopentadithiophene, but that the copolymers show clear, high bisignate Cotton effects, indicative for a supramolecular stacking. Therefore, it can be concluded that we have successfully introduced supramolecular stacking in poly(cyclopentadithiophene)s, without disrupting the conjugation or limiting the solubility and processability.

A last class of polymers studied are substituted poly(thieno[3,2-*b*]thiophenes) (PTTs). The research was focused on the development of PTTs which combine good solubility (and consequently processability) and the possibility of self-organize into highly ordered, lamellar supramolecular structures composed of planar, strongly conjugated polymer strands. Regioregular HT-P3ATs were chosen as a lead: these molecules are present as (very soluble) random-coils in solution, from which they planarize and stack upon transition to film. The origin of this behavior is the subtle interplay between steric repulsions caused by the alkyl substituent and the π-stacking. As a consequence, the choice of the proper substituent is of crucial importance.

Applied on PTTs, it could be concluded from UV-vis, CD and emission spectroscopy that dialkoxy-substituted PTTs do not show this behavior: already in good solvents, they adopt a rigid, planar conformation, which reduces their solubility and possibility to self-organize. Their strong tendency to planarize can be explained by the presence of S-O interactions and the reduced steric hindrance between the O-atom and the neighboring TT moiety (Figure 4). Dialkyl-substituted PTTs, on the other hand, show good solubilities but very poor conjugation lengths, regardless from the conditions in which they are present (good or poor solvent, film). The difficulty these polymers experience to planarize (and stack) can be attributed to the very large steric hindrance between the methylene groups of the alkyl substituents and the neighboring TT units. It is clear that both polymers lack the delicate equilibrium between repulsive and attractive forces, required to obtain the targeted behavior: while dialkoxy-substituted PTTs show too strong interactions, dialkyl-substituted PTTs suffer from too much steric hindrance. Therefore, PTTs, bearing substituents which result in an intermediate situation, were developed. This was accomplished in two ways: either by alternatingly copolymerizing dialkyl- and dialkoxy-substituted PTTs, or by using thioalkyl substituents. The choice of thioalkyl substituents is motivated by the fact that the van der Waals radius of an S-atom is intermediate between that of an O-atom and a methylene group and that therefore intermediate steric hindrance can be expected as well. Moreover, the strength of S-S interactions is usually smaller than of S-O interactions.
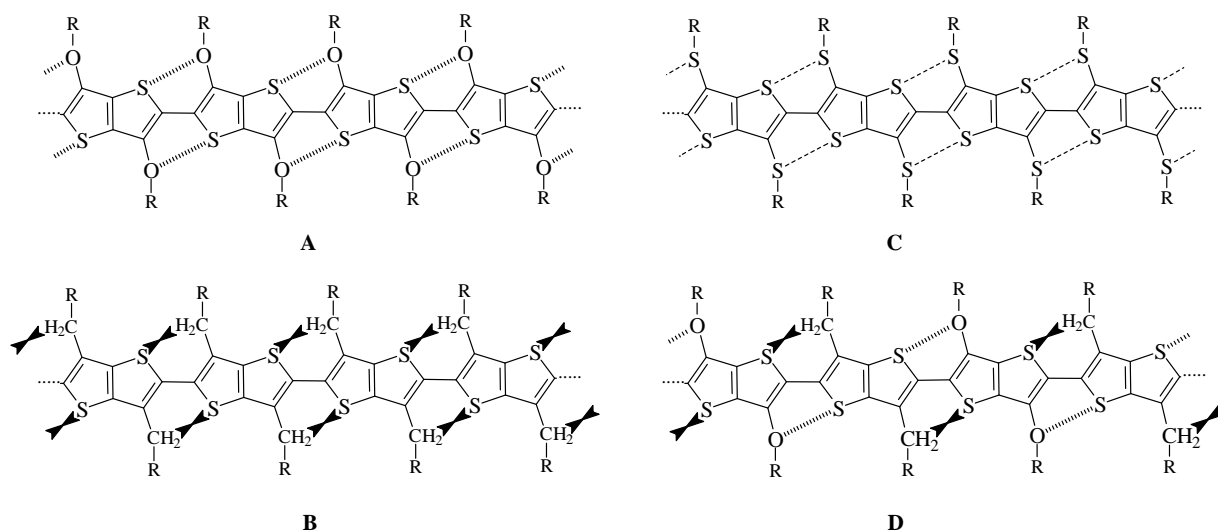
**Figure 4.** Attractive versus repulsive interaction in poly(thieno[3,2-*b*]thiophene)s: A) dialkoxy-substituted PTTs, B) dialkyl-substituted PTTs, C) dialkylthio-substituted PTTs and D) poly(dialkoxy-TT-alt- dialkyl-TT)s.

UV-vis, CD and fluorescence spectroscopy, together with DSC experiments clearly demonstrated that this approach resulted in polymers which are present as random-coils in good solvents, from which they planarize and stack upon transition to film. In this way, highly ordered structures could be obtained. The advantages of these substituted PTTs compared with HT-P3ATs are the important red-shift (60 nm), reflecting the presence of significant higher conjugation lengths, and the increased stability of the oxidized state.

**Faraday measurements**

Faraday rotaton measurements were carried at Tucson, Arizona as well as in Leuven, using analoguous instrumental set-ups fully described in the attached paper (P. Gangopadhyay, J. Phys. Chem. Dalton Festschrift, to be published) and presented in Fig. 5.
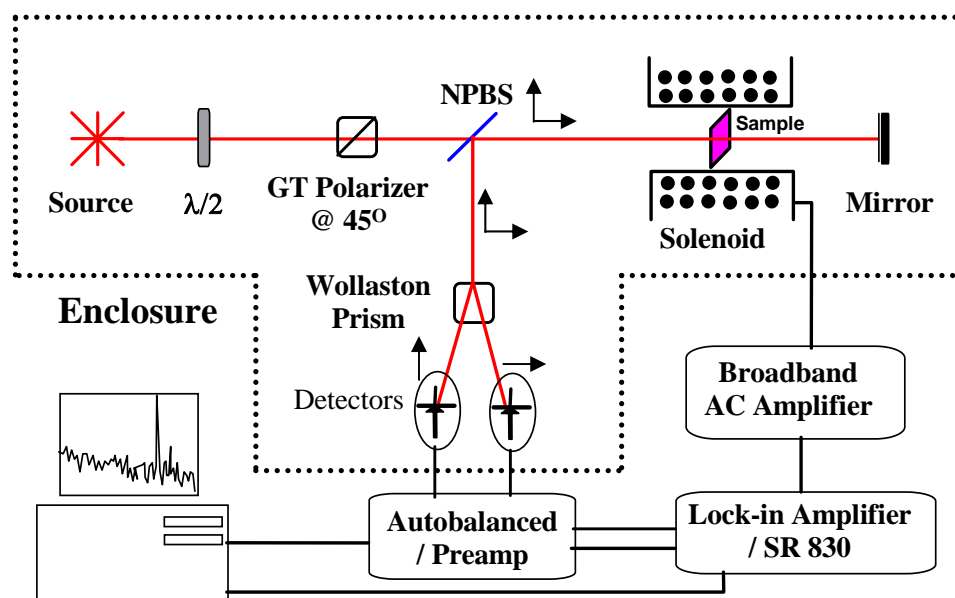


**Figure 5.** Experimental setup and the polarization states at each location: vertical, in-plane polarization; horizontal, out-of-plane polarization, red solid line is the laser beam and NPBS is a non polarizing beam splitter.

Faraday rotation measurements were done on multiple spun coat films of regioregular poly(3-dodecylthiophene) (RRP3DT) and regioregular poly(hexylthiophene) (RRP3HT) and their (commercially obtained) regiorandom counter parts. The Verdet constants calculated from the measured Faraday rotation are shown in table 1.

**Table 1.** Verdet constant ($10^4$ deg/Tm) of polymers RRP3DT and RRP3HT measured at different wavelengths. Typically 200 nm to 1 µm films are used for these measurements.

|  | 532 nm | 633 nm | 670 nm | 980 nm | 1310 nm | 1550 nm |
|---|---|---|---|---|---|---|
| RRP3DT | + 2.06 | + 2.6 | + 2.2 | + 1.6 | + 1.2 | + 0.85 |
| RRP3HT (Spun coat) | + 6.25 | + 4.42 | + 4.02 | + 2.01 | + 1.04 | + 0.84 |
| RRP3HT (Melt Processed) | - | - | + 0.60 | + 0.43 | + 0.21 | - |

The regiorandom derivatives are either Faraday inactive or the rotation is below the detection limit of our setup. The signs of Verdet constants in Table 1 do not carry any significance in an absolute sense. Within measurement error both the polythiophene derivatives show quite similar Faraday activity. To further investigate the dependence of Faraday rotation on the crystallinity and the lamellae type structure of these polymers, films were subjected to different processing conditions followed by rigorous Faraday rotation measurements. Polymer crystallization into a film from solution is a very complex exothermic process largely controlled by its thickness along with other factors such as, solubility, spin casting temperature, heat transfer coefficient, heat capacity etc. The crystallinity and crystal domain orientation of such films are known to be dependent not only on regioregularity, molecular weight but also on the processing conditions. In order to alter the crystallinity of the spun coat films we subjected the spun coat films (i) to melting at a temperature 30 °C higher than the melting points of each polymer and subsequently cooled it down with a slow cooling rate of about < 1 °C / minute and (ii) to melting at a temperature as in (i) with subsequent quick quenching at – 77 °C. Faraday rotation disappeared completely from the films of both RRP3DT and RRP3HT prepared using the method described in (ii). We have also observed that Faraday rotation from 1 μm thick films of RRP3DT decreases drastically upon melt processing following (i) and at the bottom of the detection limit of our setup. Disappearance of the "shoulders" in the absorption spectrum from these films indicates a possible collapse of the lamellae structure. However, Faraday rotation from melt-processed films as prepared and from spun films of RRP3HT could be measured. Although the Verdet constant measured from melt processed films of RRP3HT is considerably lower (~ 6000 °/Tm at 670 nm) than that of the spun coat films (~ 40000 °/Tm at 670 nm), it is easier to achieve larger rotation from melt processed thick films, a key element in any magneto-optical applications such as, isolators or magnetic field sensors. These results indicate the great importance of the supramolecular structure the role of which is at yet not completely understood. A striking example of the importance of supramolecular structure is the Faraday rotation of poly(dioctylcyclopentadithiophene) where the initial spin cast film is deeply blue colored and highly Faraday active (V = 2.5 $10^5$ deg/Tm @ 670 nm) while gradually transforming into a purple phase *without* any Faraday activity. These phase changes by film processing, e.g. annealing, are also confirmed by small angle X-ray diffraction.

## 2. Organic magnetism

In an effort to elucidate the mechanism of the large Faraday rotation in polythiophenes we did extensive magnetic measurements (SQUID) on poly(3-dodecyl)thiophene with a length of 70 monomers and with regioregularity for the chain (without the head-group) > 99% as obtained from 1H-NMR. Regiorandom P3DT with 50% H-T coupling) of similar molecular weight was used to compare the effects of regioregularity. On investigation of the magnetic properties, we found that the regioregular polythiophenes has a low temperature magnetically ordered phase (Weiss temperature, $\theta = 10.2$ K) which is not only stable under ambient conditions but also has a very large spin quantum number (S > 8000) whereas the regiorandom polymer was found to be barely paramagnetic. This is the first example of a pristine organic polymer showing a ferromagnetic phase and opens our work to the field of organic magnets. This is also the first indication for the crucial role of regioregularity. Although it is known that regioregularity improves both optical and electronic properties of pristine polythiophene derivatives, it has never been addressed with respect to magnetic properties. We also investigated by AFM techniques the structure of the films prepared from regioregular poly(3-dodecyl)thiophene. Regioregular polythiophene chains usually stack into organized 3 dimensional structures giving its optical and electronic excitations some interchain character. In polymers with a relatively low degree of polymerization flatter thiophene ring configurations and longer π-conjugation length are facilitated, further increasing at lower temperature. To our surprise we found that our regioregular poly(3-dodecyl)thiophene forms *doughnut shaped* nanostructures (Figure 6) unlike the rod and worm shaped structure previously reported albeit with larger chain lengths ( > 200 monomers). Atomic force microscopy (AFM) topographic images show that the toroid forming the doughnut has a maximum of 9.2 nm and 22 nm as its tube and inner diameters, respectively. Although doughnuts with smaller dimensions were present, no other shape was observed. Regiorandom poly(3-dodecyl)thiophene was found to form fibrous structures under similar sample preparation conditions, again showing the all-important role of regioregularity, or conjugation length.
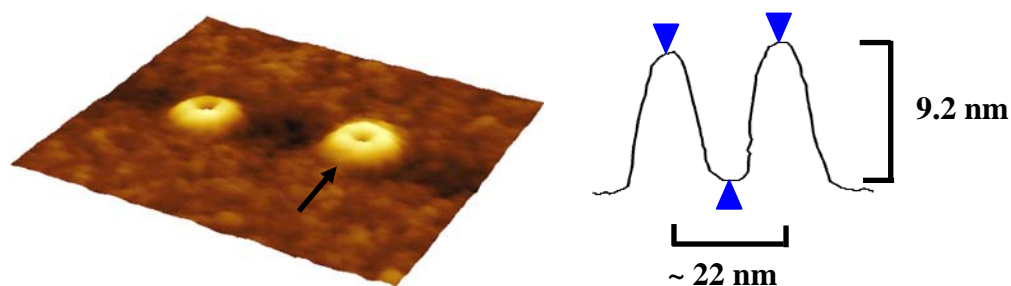


**Figure 6.**     False color AFM topographic image of regioregular poly(3-dodecyl)thiophene doughnuts. The scan line is a vertical cross section of the doughnut indicated by an arrow.

**Publications (partly) resulting from this project**

G. Koeckelberghs *et al.*, *Macromolecules*, **2007**, *40*, 4173-4181

G. Koeckelberghs *et al.*, *Macromolecules*, **2007**, *40*, 8142-8150

Lieven De Cremer *et.al.*, *Macromolecules*, **2008**, *41*, 568-578

Lieven De Cremer *et.al.*, *Macromolecules***, 2008***, 41*, 591-598

Marnix Vangheluwe *et.al.*, *Macromolecules***, 2008***, 41*, 1041-1044

David Cornelis *et.al.*, *Chem. Mater.* **2008**, *20*, 2133-2143

Palash Gangopadhyay *et.al.*, *J. Phys. Chem.* (Dalton Festschrift), **2008** to be published

Palash Gangopadhyay *et.al.*, *ACS Symposium*, 236th ACS National Meeting, **2008** (Invited Tutorial contribution, Andre Persoons)

Palash Gangopadhyay *et.al.*, *Angewandte Chemie IE*, **2008** submitted

**PS** The research on organic solar cells using our regioregular $\pi$-conjugated polythiophenes is continued at the University of Arizona, College of Optical Sciences, under the direction of Dr. J. Thomas. New (soft) lithographic techniques are developed to produce functional gratings in polythiophenes polymer films.